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DERWENT-WEEK: 200420
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TITLE: Curable resin composition for fine shaped
molding used
having
for precision equipment, contains compound
alicyclic hydrocarbon structure and radical
polymerizable
group, and polymerization initiator

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BASIC-ABSTRACT:

NOVELTY - A curable resin composition contains a compound having an
alicyclic
hydrocarbon structure and a radical polymerizable group, and a
polymerization
initiator.

DESCRIPTION - INDEPENDENT CLAIMS are included for the following:

(1) manufacture of fine shaped molding;

(2) fine shaping molding; and

(3) precision equipment.

USE - For fine shaped molding used for precision equipment. The

moldings are

components such as Fresnel lens, lenticular lens, micro lens, prism

sheet,

light reflecting plate, light diffusion board and diffraction grating

(all

claimed).

ADVANTAGE - The curable resin composition is excellent in fine

shaping

property, and enables to obtain molding with excellent strength and

heat

resistance. The molding is obtained by preventing contraction during

hardening, residual of gas bubble, destruction of film during

shaping, peeling

of film, shape collapse and distortion.

EQUIVALENT-ABSTRACTS:

POLYMERS

Preferred Composition: The alicyclic hydrocarbon structure is

monocyclic, and

polycyclic having more than bicyclic structure. The radical

polymerizable

groups are chosen from meth acryloyl group, meth acrylamide group and

vinyl

radical. The resin composition further contains a compound having

polymerizable groups, aromatic group and heterocyclic group. The

polymerization initiator is photo initiator, heat polymerization

initiator or

their mixtures. The polymerization initiator is organic peroxide

having

thermal decomposition temperature of 60 degrees or more.

TITLE-TERMS: CURE RESIN COMPOSITION FINE SHAPE MOULD PRECISION

EQUIPMENT

CONTAIN COMPOUND ALICYCLIC HYDROCARBON STRUCTURE RADICAL

POLYMERISE

GROUP INITIATE

DERWENT-CLASS: A14 A32 A89 G06 L03 U14

CPI-CODES: A08-C01; A12-L00L; A12-L02D; G06-D04; G06-F03C; G06-F03D;
L03-G02;

EPI-CODES: U14-K01A1C;

ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1]
2004 ; G0908 G0873 G0817 D01 D51 D54 D57 D63 D26 D12 D10 D14 D13
D17*R
D07 D31 D33 D76 D78 D58 D93 F90 F41 G0817*R G0964 D12*R F70*R F94
F70;

H0022 H0011; H0033 H0011; L9999 L2528 L2506; M9999 M2073;
K9869 K9847

K9790; S9999 S1434;

Polymer Index [1.2]

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B4091*R

B3838 B3747; B9999 B4682 B4568; B9999 B5550 B5505; B9999

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B3747; ND01;

Polymer Index [1.3]

2004 ; D01 F48; C999 C088*R C000; C999 C340; C999 C293;

Polymer Index [1.4]

2004 ; C999 C077 C000; C999 C340; C999 C293;

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(54) 発明の名称] 硬化型樹脂組成物および積層成形品

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(19) 日本国特許庁 (J P)

(A) 多官能(4×7)ポリマー(分子量700以上)
 (B) 多官能(4×7)ポリマー(分子量700以上)
 (C) 単官能7-ポリマー: 5~44重量%
 (D) 光硬化開始剤

からなる光硬化樹脂組成物の樹脂層を基体上に形成し、その樹脂層は繰り返し形状を有する回折格子が提案されている。その表面には、反射防止層あるいは反射層を形成する。繰り返し形状を有する樹脂層は、ガラス、金属、プラスチックなどの型を用いて注法により成形

され、得られた回折格子の耐久性が優れていることが特徴とされている。この製造方法では、次のような問題点がある。

きく。注成型により、設計通りの微小な形状とすること
とは非常に困難である。成分(A)の数平均分子量は70
0~5,000(実例例では860~3,000)が好ましいとされて
いるように、分子量が大きく、実例例の耐久試験①は70
℃の低温で実施されているのみであり、高温での耐熱性

【特許文獻1】特開平6-16721号公報
【特許文獻2】特開平6-263831号公報
【特許文獻3】特開平7-128503号公報

【特許文獻4】特開平6-208008号公報
【特許文獻5】特開平6-67004号公報
【特許文獻6】特開平5-196808号公報
【特許文獻7】特開平11-42649号公報
【特許文獻8】特開平6-67571号公報

【0020】
【発明が解決しようとする課題】上記した従来の公知技術は、硬化型樹脂組成物を用いた微細形成形状を製造する方法として、下記のように分類できる。

熱硬化させる製造方法。
 ①熱に安定な樹脂組成物を成形型に注入したのち、光または熱を押し当てたまま、または押し当てたのち、光または熱を硬化する製造方法。

③硬化型樹脂組成物を基料に滴下または塗布し、フラスコを通して部分的に光硬化をさせたのち、未硬化部分を除去する製造方法。

【0021】上記した①～③の製造方法では、硬化収縮率が大きいため、設計形状の角部、先端部、底面などに

において、設計通りの精密な形状を成形することが非常に困難であり、硬化時に基材との割離が発生し易く、硬化物中に歪みが発生するという共通した問題点がある。また、十分な強度と耐熱性を有する成形物を得ることも困難である。

【0022】上記の方法における注量成形では、注入

【0037】本発明において、「多環式の脂環族炭化水素骨格」と、1個のラジカル重合性基を有する化合物」

(以下、化合物(a3)と表記する。)を反応性希釈剤として有効に使用する場合には、化合物(a1)と化合物

(a3) との配合比は100:0~60:40(重量部)であり、
母ましかは100:0~65:35(重量部)である。

明の硬化型樹脂組成物の粘度調整あるいは硬化物の特性の調整や向上が必要な場合には、前記したように、脂環式炭化水素骨格を有さず、かつラジカル重合性を有する

炭化合物(成分A')が併用されてよい。そのような成分(A')の化合物として、例えば、上記したラジカル重合性基を有する脂肪族系、芳香族系、複素環系など

の化合物が得られる。成分(A')においても、ラジカル重合性基として(メタ)アクリロイル基、(メタ)アクリルアミド基及びニル基から選択され

5.2個以上の基を有する化合物の使用が好ましい。
【0039】(メタ)アリロイル基を2個以上有する脂肪族系化合物の具体例としては、エチレンアリール

(X%) 77リットル、1.2-3.3g/L、3-7g/L
77リットル、1.4-7g/L、(X%) 77リットル、ネオペンチルグリコール

(X) 70-1-1, 70-1-2, 70-1-3, 70-1-4, 70-1-5, 70-1-6, 70-1-7, 70-1-8, 70-1-9, 70-1-10, 70-1-11, 70-1-12, 70-1-13, 70-1-14, 70-1-15, 70-1-16, 70-1-17, 70-1-18, 70-1-19, 70-1-20, 70-1-21, 70-1-22, 70-1-23, 70-1-24, 70-1-25, 70-1-26, 70-1-27, 70-1-28, 70-1-29, 70-1-30, 70-1-31, 70-1-32, 70-1-33, 70-1-34, 70-1-35, 70-1-36, 70-1-37, 70-1-38, 70-1-39, 70-1-40, 70-1-41, 70-1-42, 70-1-43, 70-1-44, 70-1-45, 70-1-46, 70-1-47, 70-1-48, 70-1-49, 70-1-50, 70-1-51, 70-1-52, 70-1-53, 70-1-54, 70-1-55, 70-1-56, 70-1-57, 70-1-58, 70-1-59, 70-1-60, 70-1-61, 70-1-62, 70-1-63, 70-1-64, 70-1-65, 70-1-66, 70-1-67, 70-1-68, 70-1-69, 70-1-70, 70-1-71, 70-1-72, 70-1-73, 70-1-74, 70-1-75, 70-1-76, 70-1-77, 70-1-78, 70-1-79, 70-1-80, 70-1-81, 70-1-82, 70-1-83, 70-1-84, 70-1-85, 70-1-86, 70-1-87, 70-1-88, 70-1-89, 70-1-90, 70-1-91, 70-1-92, 70-1-93, 70-1-94, 70-1-95, 70-1-96, 70-1-97, 70-1-98, 70-1-99, 70-1-100.

[illegible]

1. 2. 3. 4. 5. 6. 7. 8. 9. 10. 11. 12. 13. 14. 15. 16. 17. 18. 19. 20. 21. 22. 23. 24. 25. 26. 27. 28. 29. 30. 31. 32. 33. 34. 35. 36. 37. 38. 39. 40. 41. 42. 43. 44. 45. 46. 47. 48. 49. 50. 51. 52. 53. 54. 55. 56. 57. 58. 59. 60. 61. 62. 63. 64. 65. 66. 67. 68. 69. 70. 71. 72. 73. 74. 75. 76. 77. 78. 79. 80. 81. 82. 83. 84. 85. 86. 87. 88. 89. 90. 91. 92. 93. 94. 95. 96. 97. 98. 99. 100. 101. 102. 103. 104. 105. 106. 107. 108. 109. 110. 111. 112. 113. 114. 115. 116. 117. 118. 119. 120. 121. 122. 123. 124. 125. 126. 127. 128. 129. 130. 131. 132. 133. 134. 135. 136. 137. 138. 139. 140. 141. 142. 143. 144. 145. 146. 147. 148. 149. 150. 151. 152. 153. 154. 155. 156. 157. 158. 159. 160. 161. 162. 163. 164. 165. 166. 167. 168. 169. 170. 171. 172. 173. 174. 175. 176. 177. 178. 179. 180. 181. 182. 183. 184. 185. 186. 187. 188. 189. 190. 191. 192. 193. 194. 195. 196. 197. 198. 199. 200. 201. 202. 203. 204. 205. 206. 207. 208. 209. 210. 211. 212. 213. 214. 215. 216. 217. 218. 219. 220. 221. 222. 223. 224. 225. 226. 227. 228. 229. 230. 231. 232. 233. 234. 235. 236. 237. 238. 239. 240. 241. 242. 243. 244. 245. 246. 247. 248. 249. 250. 251. 252. 253. 254. 255. 256. 257. 258. 259. 260. 261. 262. 263. 264. 265. 266. 267. 268. 269. 270. 271. 272. 273. 274. 275. 276. 277. 278. 279. 280. 281. 282. 283. 284. 285. 286. 287. 288. 289. 290. 291. 292. 293. 294. 295. 296. 297. 298. 299. 300. 301. 302. 303. 304. 305. 306. 307. 308. 309. 310. 311. 312. 313. 314. 315. 316. 317. 318. 319. 320. 321. 322. 323. 324. 325. 326. 327. 328. 329. 330. 331. 332. 333. 334. 335. 336. 337. 338. 339. 340. 341. 342. 343. 344. 345. 346. 347. 348. 349. 350. 351. 352. 353. 354. 355. 356. 357. 358. 359. 360. 361. 362. 363. 364. 365. 366. 367. 368. 369. 370. 371. 372. 373. 374. 375. 376. 377. 378. 379. 380. 381. 382. 383. 384. 385. 386. 387. 388. 389. 390. 391. 392. 393. 394. 395. 396. 397. 398. 399. 400. 401. 402. 403. 404. 405. 406. 407. 408. 409. 410. 411. 412. 413. 414. 415. 416. 417. 418. 419. 420. 421. 422. 423. 424. 425. 426. 427. 428. 429. 430. 431. 432. 433. 434. 435. 436. 437. 438. 439. 440. 441. 442. 443. 444. 445. 446. 447. 448. 449. 450. 451. 452. 453. 454. 455. 456. 457. 458. 459. 460. 461. 462. 463. 464. 465. 466. 467. 468. 469. 470. 471. 472. 473. 474. 475. 476. 477. 478. 479. 480. 481. 482. 483. 484. 485. 486. 487. 488. 489. 490. 491. 492. 493. 494. 495. 496. 497. 498. 499. 500. 501. 502. 503. 504. 505. 506. 507. 508. 509. 510. 511. 512. 513. 514. 515. 516. 517. 518. 519. 520. 521. 522. 523. 524. 525. 526. 527. 528. 529. 530. 531. 532. 533. 534. 535. 536. 537. 538. 539. 540. 541. 542. 543. 544. 545. 546. 547. 548. 549. 550. 551. 552. 553. 554. 555. 556. 557. 558. 559. 560. 561. 562. 563. 564. 565. 566. 567. 568. 569. 570. 571. 572. 573. 574. 575. 576. 577. 578. 579. 580. 581. 582. 583. 584. 585. 586. 587. 588. 589. 590. 591. 592. 593. 594. 595. 596. 597. 598. 599. 600. 601. 602. 603. 604. 605. 606. 607. 608. 609. 610. 611. 612. 613. 614. 615. 616. 617. 618. 619. 620. 621. 622. 623. 624. 625. 626. 627. 628. 629. 630. 631. 632. 633. 634. 635. 636. 637. 638. 639. 640. 641. 642. 643. 644. 645. 646. 647. 648. 649. 650. 651. 652. 653. 654. 655. 656. 657. 658. 659. 660. 661. 662. 663. 664. 665. 666. 667. 668. 669. 670. 671. 672. 673. 674. 675. 676. 677. 678. 679. 680. 681. 682. 683. 684. 685. 686. 687. 688. 689. 690. 691. 692. 693. 694. 695. 696. 697. 698. 699. 700. 701. 702. 703. 704. 705. 706. 707. 708. 709. 710. 711. 712. 713. 714. 715. 716. 717. 718. 719. 720. 721. 722. 723. 724. 725. 726. 727. 728. 729. 730. 731. 732. 733. 734. 735. 736. 737. 738. 739. 740. 741. 742. 743. 744. 745. 746. 747. 748. 749. 750. 751. 752. 753. 754. 755. 756. 757. 758. 759. 760. 761. 762. 763. 764. 765. 766. 767. 768. 769. 770. 771. 772. 773. 774. 775. 776. 777. 778. 779. 780. 781. 782. 783. 784. 785. 786. 787. 788. 789. 790. 791. 792. 793. 794. 795. 796. 797. 798. 799. 800. 801. 802. 803. 804. 805. 806. 807. 808. 809. 810. 811. 812. 813. 814. 815. 816. 817. 818. 819. 820. 821. 822. 823. 824. 825. 826. 827. 828. 829. 830. 831. 832. 833. 834. 835. 836. 837. 838. 839. 840.

(イ) 2000年12月31日現在、当社の保有する株式の総数は、1,000,000株であり、そのうち、当社の関係者が保有する株式の総数は、100,000株である。

[illegible]

【0040】(メタ)アクリル基を2個以上有する芳香族系化合物の具体例としては、ビスフェノールAおよびそのエポキシ化体である。

$\varphi(x) = \begin{cases} 1 & x \in \mathbb{R} \\ 0 & x \notin \mathbb{R} \end{cases}$

[illegible]

シ(×9) アクリル酸付加物、エスアエノールAおよび
エスア(クリシシロキエチルエーテル) およびエス
ア(クリシシロアロキエチルエーテル) のシ(×9) アクリル

[illegible]

【0033】成分(A)の化合物は、ラジカル重合性基を分子中に2個以上有することが好ましく、2個以上のラジカル重合性基を上記したラジカル重合性基の群から

用では、感形される膠粘性や耐熱性が必ずしも十分なものでない。ラジカル重合性基が1個の化合物のみで感形される。その感形剤は、その感形剤として用いられるものとはならない。尚、同一分子中に有する2個以上のラ

シカル重合体は、それと結合した金属イオン、同一分子のシカル重合基を1個有する化合物は、反応性希釈剤として有効に使用することができる。

【0034】硬化性（重合性）や硬化物の物性の観点から、好ましい2個以上のラジカル重合性基は、(X₂)

基、ピニール基、及びピニール基からなる群から選択され、より好ましくは(メタ)アクリロイル基、(メタ)アクリル基、及びピニール基からなる群から選択され、より好ましくは(メタ)アクリロイル

【0035】本発明の成分(A)である化合物におい

 $\text{CH}_3\text{CO}-$, $(\text{C}(\text{H})_2)_2\text{O}$, $-\text{O}-$, $-(\text{CH}_2)_2\text{O}-$, $-$, $-(\text{CH}_2)_2\text{O}-$, $-$, $-(\text{CH}_2)_2\text{O}-$, $-$, $-(\text{CH}_2)_2\text{O}-$, $-$, $-(\text{CH}_2)_2\text{O}-$. $-\text{CH}_3$
$$\begin{aligned} & (\text{CH}_3)_2\text{C}=\text{O}, -\text{O}(\text{CH}_2)_4\text{O}-, -\text{OCH}_2\text{CH} \\ & (\text{OH})\text{CH}_2\text{O}-, -\text{CH}_2-, -(\text{CH}_2)_2-, - \\ & (\text{CH}_2)_3- \end{aligned}$$

いでもよい。連結基の炭素原子数が7以上となると、微細な成形性や耐熱性に問題がでるので好ましくない。

環炭化水素骨格とラジカル重合性基を有する化合物のうち、少なくとも「2環式以上、好ましくは3環式以上」の多環式脂環炭化水素骨格と、上記した2環式のラ

ジカル重合性基を有する化合物」(以下、化合物(a1)と表記する。)を使用することが好ましい。このとき、「1」式の脂肪族炭化水素骨格と、1個以上のラジカル

運合性基を有する化合物」(以下、化合物(a2)と表記する。)を反応性希釈剤として有効に使用する場合に、化合物(a1)と化合物(a2)との配合比は100:0~

60:40(重量部)であり、好ましくは100:0~70:30(重量部)である。

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硬化させる方法が有利である。

【0080】光重合開始剤(成分(81))を配合した光

硬化の場合は、紫外線を照射するが一般例である。紫

外線光源としては、超高圧水銀灯、高圧水銀灯、低圧

水銀灯、メタルハライド灯、カーボンアーク灯、キセノ

灯の使用が好適である。光硬化を単純で行って完全硬化

しなくてはならないが、高圧水銀灯あるいはメタルハロ

イド灯などがあるが、

構成によっても異なるが、通常2,500〜5,000mJ/cm²であ

る。

【0081】熱重合開始剤である有機過酸化化合物(成分

(82))を配合した無熱の場合は、前記した有機過酸

化物の無分解温度以上に加熱して硬化させる。加熱時間

は通常10〜60分である。

【0082】光重合開始剤(成分(81))と有機過酸化

物(成分(82))をともに配合した光硬化と熱硬化を組

み合わせた硬化の場合は、まず、紫外線照射により、光

硬化したのち、加熱により熱硬化するのが一般的であ

る。この場合は、紫外線を光硬化により完全硬化させな

くても、熱く熱硬化により完全硬化させることができ

る。その照射した照射条件でよい。

【0083】光硬化または/および熱硬化後の硬化膜の

硬化状態は、フーリエ変換赤外線分光分析装置や化学分析

装置などを用いて測定できる。本発明の硬化型

樹脂組成物は完全を硬化する硬化条件は適宜決定すること

ができる。

【0084】続いて、上記した硬化方法によって得られ

た硬化膜に順に、押し車を適用して緻密な形状を膜形す

れば、緻密な形状が得られる。詳しくは、硬化膜

が形成された表面を加熱装置に保持しながら、緻密な形

状を与える押し車を硬化膜に押し当て、押し車の緻密形

状を硬化膜に与えながら、本発明において

は、硬化膜は完全硬化されてより膜形され易い良好な膜物

性を有しているため、基板からの剥離や破壊あるいは膜

の形状崩壊などを起こすことなく、緻密な形状を良好

である。加熱装置下で膜形するのには、硬化膜を少し軟化

させて膜形をより容易にするためである。

【0085】押し車による緻密な膜形成は、本発明の硬

化型樹脂組成物の樹脂成分(成分(A))または成分

(A')と成分(A'')の成分組成によっても異なる

が、通常、150〜300℃、好ましくは、200〜300℃の加熱

温度下で、圧力は100〜400mPa、好ましくは、200〜300m

Paであり、時間は5〜60秒、好ましくは、20〜50秒であ

る。

【0086】(方法11)本発明の別の緻密な膜形成物の

膜形状としては、紫外線照射による硬化(不完全硬

化)と、完全を硬化膜形成後に膜形し、熱硬化によ

り完全硬化する方法である。この方法は、完全硬化膜の

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場合よりも、緩和な膜形成条件が採用できることに特長が

ある。

【0087】詳しくは、方法1と同様にして、まず基版

上に形成された表面を紫外線を照射して不完全硬化せ

る。この光硬化では、硬化膜の表面の粘着性がなくな

り、脱形時、膜破壊、膜剥離、形状崩壊が発生しない液

特性を中止する。光硬化を中止する。不完全硬化膜は、膜

形成され易い良好な膜物性を有しているのて、緻密な形状

を精密に膜形できる。紫外線照射量は、通常、500〜200

0mJ/cm²の範囲であり、最適条件を選択すればよい。

【0088】続いて、不完全硬化膜上に、押し車を使用し

て緻密な形状を膜形する。即ち、不完全硬化膜が形成

された表面を加熱装置に保持しながら、緻密な形状を与

える押し車を不完全硬化膜に押し当て、押し車の緻密形状

を完全硬化膜に与えながら、本発明において、膜形され

易い良好な膜物性を有しているため、基板からの剥離や破

壊あるいは形状崩壊などを起こすことなく、緻密な形状

を良好に膜形でき、また膜形後の押し車の弾性も良好

である。

【0089】この方法においても、加熱装置下で膜形加

工するのには、不完全硬化膜を少し軟化させる。膜形をよ

り容易にするためである。この方法においては、硬化型

樹脂組成物中には、光重合開始剤とともに、熱重合開始剤

が配合されている。加熱装置下に保持しながら膜形され

るのて、熱重合開始剤としては、高度分解型の有機過酸化

物の配合が好ましく、特に、モノテラールハロイド

キナイドやジニル・モノキナイドの配合が特に好まし

い。

【0090】押し車による緻密な膜形成は、100〜150℃

の加熱装置下で、加熱時間は数分〜20分であり、圧

力は比較的低圧でよく、通常、50〜200kPaの範囲であ

る。

【0091】最後に、膜形された不完全硬化膜を熱によ

り完全硬化させる。即ち、加熱することによって、膜形

された不完全硬化膜中に残存する溶剤成分を完全

きに硬化させる。このため、加熱硬化による膜形された

完全硬化膜の硬化収縮は殆どなく、膜形形状がそのまま

保持され、しかも耐熱性に優れた膜形成物とすること

ができる。また、膜形成物の形状崩壊や、剥離、破壊

なども発生しない。加熱条件は、有機過酸化化合物の種類や

配合量などによって異なるが、通常、加熱温度は150〜2

50℃であり、加熱時間は数分〜60分である。

【0092】以上のような方法1および方法11に従って

製造された本発明の緻密な膜形成物の特性は、硬化時の取組

み、脱形時、膜破壊、膜剥離、形状崩壊、形状崩壊

および溶剤などの問題がなく、押し車の緻密な形状が精

確よく転写されている。押し車の膜形成は、特に制限

はないが、溶剤(溶き)および溶(スリッ)とも異なる

の緻密な形状であっても、95%以上の極めて優れた膜

転写で膜形される。また、本発明の緻密な膜形成物の熱

い

い

い

る。図1は、樹脂成形品を250℃で1時間加熱して

る。変形、形状崩れ、軟縮、割傷などは起こらず、高温

での形状保持にも優れている。従って、樹脂成形品

に、高温条件下で、蒸着法、スパッタリング法、イオン

・プラズマ処理などの常法により、金属膜の蒸着

を行って、微細な形状は成形することになり、さら

ら、本発明の樹脂成形品は強度や基板との密着性に

も優れている。

【0093】本発明の硬化樹脂組成物を用いて製造さ

れた樹脂成形品は、上記したような特長を活かし

て、フィルム、レンズ、レンズケース、マイクロ

デバイス、ラミネーション、光反射板、光散板、回折格

子などの部品や部材として、光学機器、液晶表示機器、

プロセッサ内蔵機器、通信機器などの多種多様な構

造機器に使用することができ、以下の実施例により、

本発明により具体的に説明するが、本発明は実施例に限

定されるものではない。

【0094】

【実施例】試験と測定は次の方法にしたがった。

<硬化試験> 実施例1〜4および比較例1〜7は、0.05×

横、0.05×厚さ1.0mmの表面に、深さ1mm×長さ0.05×

用いて、押し圧下での成形加工試験を行った。深さ0.05×

1mmの断面が三角形の凸形状を配列した樹脂用金型を

用いて、押し圧下での成形加工試験を行った。深さ0.05×

1mmの断面が三角形の凸形状を配列した樹脂用金型を

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1mmの断面が三角形の凸形状を配列した樹脂用金型を

用いて、押し圧下での成形加工試験を行った。深さ0.05×

定の条件下で硬化硬化を行ったこと、および樹脂硬化方法が完

全に硬化状態にあることを確認して硬化硬化の測定は硬化後

に行なった以外は、上記方法と同様にして試験評価を行っ

た。

【0097】<実施例1> スチロール/ポリスチレン/5.0%

2.1, 0.4% 4-ベンゾイル/ポリスチレン/7.0%, 1.4-スチ

ロキシ/ポリスチレン/ポリスチレン/3.0%および

（特）製品：0.80gを混合、溶解して硬化樹脂組成物

（1）を調製した。この樹脂組成物（1）を、スピン

コートを用いて、ガラス基板上に塗布した。樹脂組成物

（1）の塗布厚さは4μmであった。この塗布面に炭

素コートを用いて、ガラス基板上に塗布した。この塗布面に炭

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素コートを用いて、ガラス基板上に塗布した。この塗布面に炭

いてガラス基板の上に塗布した。続いて、室温に放置し、さらに、少し減圧下で50℃に加熱して、各層を溶剤を揮発除去し、厚3.3 μ mの樹脂組成物（V1）の塗布膜を得た。この塗布膜に紫外線を1,200mJ/cm²となるまで照射し、粘着性のない光硬化樹脂膜とした。次に、膜形用金重を用いて、140℃で15秒間、180mPaの加圧下で光硬化樹脂膜の表面に成形し、金重を離型した。金重の離型性は良好であった。続いて、200℃で20分間加熱して、膜形された光/熱硬化樹脂膜とした。膜形された光/熱硬化樹脂膜は、前記した測定により、完全硬化していることを確認した。膜形の転写率を測定した結果は95%であり、非常に良好な値を得た。膜形された硬化樹脂膜の表面に、常法にしたがって、アルミニウムを厚さ約0.1 μ mとなるように蒸着して、光反射板とした。この光反射板の表面形状を触針式表面凹凸計を用いて測定したところ、三角形の崩れは全く見られなかった。

【0110】
 発明の効果を】本発明の硬化型樹脂組成物により、硬化時の収縮、未完全硬化、気泡残留、ならびに膜形時の膜破壊、膜剥離、形状崩れおよび歪みなどの問題を引き起こさなく、膜細形状が精度よく膜形された。十分な強度と耐熱性を有する膜細膜形成物を簡単に製造できる。

ルネラルアセテート：10.0gを混合、溶解して硬化型樹脂組成物（V）溶液を調製した。この樹脂組成物（V）溶液を、スピンコーターを用いてガラス基板の上に塗布した。続いて、室温に放置し、さらに、少し減圧下で50℃に加熱して、各層を溶剤を揮発除去し、厚3.3 μ mの樹脂組成物（V1）の塗布膜を得た。この塗布膜を、120℃で20分間、さらに150℃で20分間加熱して、熱硬化樹脂膜とした。熱硬化樹脂膜は、前記した測定により、完全硬化していることを確認した。次に、膜形用金重を用いて、250℃において30秒間、250mPaの加圧下で熱硬化樹脂膜の表面に成形し、金重を離型した。金重の離型性は良好であった。膜形の転写率を測定した結果は95%であり、非常に良好な値を得た。膜形された硬化樹脂膜の表面に、常法にしたがって、アルミニウムを厚さ約0.1 μ mとなるように蒸着して、光反射板とした。この光反射板の表面形状を触針式表面凹凸計を用いて測定したところ、三角形の崩れは全く見られなかった。

【0109】＜実施例6＞ジメチルホルトリシクロ（5,2,1,0^a,8）テトラヒドロフラン：3.5g、アルギニート：2.1,0^a,8）テトラヒドロフラン：6.5g、ベンゾエリニート：0.3g、ジメチルホルトリシクロ：0.2gおよびエチルトリメチルシリルエーテルセグメント：10.0gを混合、溶解して硬化型樹脂組成物（V1）溶液を調製した。この樹脂組成物（V1）溶液を、スピンコーターを用

フロンティアの設計

フロンティア（参考） 4971 M33 M38 M54 M28
 M119 B402 B802 B812 B002
 A4015 B403 B404 B405 B406 B407
 A1100 M408P M452R M453R M466P
 M464Q M468R M472R B402R
 B004Q B007P B007Q B009P
 B009Q B012P B045R B048R
 B074R B075R C401 C404
 C405 C423 F403 F418 J432
 J433

* NOTICES *

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2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a hardening resin constituent, the hardening resin constituent excellent in especially detailed formativeness, and the detailed size

enlargement molded product manufactured using this constituent. In detail, it is related with the hardening resin constituent which excels [surface / after photo-curing / or and heat curing / hardened material] in detailed formativeness, and the detailed size enlargement molded product in which size enlargement of the detailed shape was carried out to the hardened material surface.

[0002]

[Description of the Prior Art] The molded product which carried out size enlargement of the detailed shape to the surface or a surface has been used using a photo-curing type or a heat-hardened type resin composition as parts and members, such as a variety of optical instruments, liquid crystal display device, projection apparatus, and optical communication equipment. As an example of representation as such parts or a member, a Fresnel lens, a lenticular lens, a micro lens, a prism sheet, a light reflection plate, an optical diffusion board, a diffraction grating, etc. can be illustrated. About manufacture of such parts or a member, various manufacturing methods for carrying out size enlargement of the minute shape have

been proposed.

[0003] In [for example] the patent documents 1 in the field of a Fresnel lens, (A) Urethane (meta) acrylate and/or epoxy (meta) acrylate, (B) Pour in ethylenic unsaturation group content compounds other than (A), (C) semicarbazide compound, and the resin composition that consists of a (C) photopolymerization initiator between a metallic mold and a transparent substrate, it is made to harden by UV irradiation, and the art of manufacturing a Fresnel lens is reported. Although the mold reproducibility of die shape is indicated that it is good and there is

little coloring after heating (100**) neglect, the value with important size of die shape, thickness of mold goods, amount of UV irradiation, etc. is not indicated. A fixed quantity of mold reproducibility has not turned and is not observed subjectively. Furthermore by this manufacturing method, there are the following problems.

[0004](Meta) Since the rate of cure shrinkage of an acrylate compound is generally about 10% (volume), its mold-release characteristics is visible to fitness apparently, but one side is not so enough as the mold reproducibility of die shape. If a nail is forced on the mold-goods surface under ordinary temperature, marks will stick, it is indicated that this scratch is recovered in 30 minutes, and this does not show hardness flexible mold goods and sufficient, but it means that heat resistance is insufficient.

[0005]In the patent documents 2 for example, Diacrylate of ester of dimethacrylate:30 - 60-% of the weight hydroxy [(2)] PIPARIN acid, and neopentyl glycol which is ethyleneoxide denaturation bisphenol A : (1) 5 - 20-% of the weight phenoxyl [(3)] ethyl, or phenoxethoxyethyl acrylate : Depending on the case, with the resinous principle which

consists of 25 to 50 % of the weight. N-vinyl pyrrolidone : (4) The ultraviolet curing type resin composition which consists of a resinous principle which added 1 to 6 % of the weight, and a photopolymerization initiator, it is made to intervene between the mold made of metal or a synthetic resin and transparent resin base which have Fresnel lens shape, and the production technology which irradiates with ultraviolet rays and forms a lens part in one is reported. There are the following problems in this manufacturing method.

[0006]Although a resinous principle (3) lowers the viscosity of a resin composition as described, and blended as a dilution monomer for avoiding the contamination of air bubbles, it does not blend like a statement, the cure shrinkage at the time of a polymerization will become large, and a mold-release characteristic will become good, but lens mold transfer nature worsens. Although having elastic force is indicated as one of the features of a hardened material, although there is elastic force in a hardened material, there is no hardness, and heat resistance is not enough.

[0007]In [for example] the patent documents 3 in the field of a lenticular lens, Thermoplastic polymer : (1) The active energy line hardening type resin composition which becomes 20 to 80 in resin composition 100 weight section (2) intramolecular from the monomer (3) photopolymerization initiator which has one or more unsaturated double bonds. After applying to one side or both sides of a sheet-shaped transparent base material (3 mm or less in thickness), a flat tip or a rolled form lens mold is stuck, a lens pattern is transferred, the composition which irradiated with and applied the activity energy line is stiffened, and the production technology which obtains a lens sheet is reported. There are the following problems in this manufacturing method.

[0008]Since a lot of thermoplastic polymer is blended (it is 20 to 80 weight section to resin

composition 100 weight section), removal of the air bubbles twisted and mixed in the coating method (the solution coating method, heating coating method, and extrusion coating method using a solvent are indicated.) is difficult. Since a lot of thermoplastic polymer (what has a linear structure) is blended, naturally heat resistance is remarkably low. Although a rolled form metallic mold with large (pitch 400micrometer, the curvature radius of 214 micrometers, a depth of 137 micrometers) lens pattern shape is used and it is described in the example that the lens pattern was transferred precisely. The state of the resin composition applied to the transparent base material is not different from thermoplastics material at all, therefore is dramatically difficult to transfer [a minute lens pattern and] especially a lens pattern of 10 micrometers or less.

[0009]for example in the patent documents 4 in the field of a micro lens -- the (A) polymer (thing malleable to (B)), and the (B) monomer (photopolymerization be possible) it is plate-like (in an example,) about the resin composition (at a room temperature, it is 10,000 poise or more) which consists of an optical start type catalyst, 0.5 mm in thickness and 5-6 cm in diameter are used, and it is a photo mask (in an example.). After irradiating with a chemical lamp through 650-micrometer [in diameter], and pitch 800micrometer, or 350-micrometer [in diameter], and pitch 390micrometer and forming a cylindrical lens part with convex. A photo mask is removed and the manufacturing method which irradiates that whole it is monotonous with the parallel beam of ultraviolet rays, stiffens a non-hard spot, and produces a plastic

microlens array is reported. There are the following problems in this manufacturing method. [0010]The above-mentioned resin composition is a resin composition which dissolved a lot of polymers (an example 50 % of the weight of polymethylmethacrylates) in the monomer, and since it is necessary to make it hyperviscosity extremely in order to consider it as plate-like, removal of the air bubbles mixed at the time of the dissolution is dramatically difficult. Since a lot of [the above-mentioned resin composition] meltable polymers (thermoplastics) are mixed, the microlens array hardened and produced is remarkably inferior to heat resistance. By the method of carrying out photo-curing of a photopolymerization monomer like acrylate through a photo mask, hardening or minute sections and especially the thing you control the size of 10 micrometers or less, and is made to harden precisely are impossible.

[0011]in [for example] the patent documents 5 in the field of a prism sheet, an active energy line hardening type resin composition (what is excellent in transparency and gives a bridge construction curing polymerization thing.) (Meta) The acrylic ester system is especially indicated to be desirable. The application process applied to a die, The laminating process which piles up a transparent base material (3 mm or less in thickness), the curing process which irradiates with and stiffens an actively energy line, and the release process which releases a molded product from mold from a die are performed. The production technology which produces the triangular prism sheet for liquid crystal displays in which many prism of the

long and slender section triangular shape whose angle of a vertical angle is 70-110 degrees was formed continuously is reported. The rate of bending flexibility of the obtained triangular prism sheet is made good [that it is 10000 - 50000 kg/cm²]. The sizes of a triangular prism are 70-90 micrometers in pitch, and 30-50 micrometers in height.

If thickness is a 4-10-inch screen, 200-500 micrometers is indicated to be good.

There are the following problems in this manufacturing method.

[0012] Although it is indicated that it had the shape as a design, in the resin composition which consists of an ingredient indicated in the example, the shape of the triangular prism after cure molding has a large rate of cure shrinkage, and in order to obtain the shape of the triangular prism to need, it produces big difficulty in the design of a forming mold. With the kind of ingredient which constitutes a resin composition, the rate of a compounding ratio, etc., in order that the rate of cure shrinkage may change a lot, the precise design of a die becomes much more difficult. In a resin composition with such a large rate of cure shrinkage, a minute-shaped prism sheet and especially the manufacture by the cure molding of a prism sheet of 10 micrometers or less are impossible.

[0013] In the field of the optical diffusion board, the manufacturing method with which hardening resin is formed, for example as shape which has refractivity on it with a transparent resin film base in the patent documents 6 is indicated as follows. Although it is supposed that not less than (200micron in thickness) about 80% of thing has preferred visible light transmission and there is no restriction in hardening resin in any way on the other hand as a transparent resin film, it is supposed from on dimensional accuracy that an ultraviolet curing type acrylic resin is especially preferred. As shape which has refractivity, the shape of boiled fish paste, the shape of many pyramids, the shape of a washboard, etc. are illustrated, and the height is made preferred [5-10 micrometers]. On the other hand, it is the grade described in the example to be ultraviolet curing type acrylic resin system ink (refractive indices 1.47 and 1.43) about hardening resin. There are the following problems in this manufacturing method.

[0014] If hardening resin is used at all, cure shrinkage is not avoided but especially the cure shrinkage of the acrylic resin of the ultraviolet curing type made desirable is large. Therefore, in order to form the shape of the refractivity to need correctly for the completely same reason with having described above, extraordinary difficulty is produced in the design of a die.

[0015] In the field of the light reflection plate, the manufacturing method of the reflector is indicated as follows, for example in the patent documents 7. The photopolymer liquid of a resist system is applied to the glass base material upper surface. It heats using heating apparatus (more than 80-100 ° x1 minute), the solvent contained in photopolymer liquid is removed, and a photosensitive resin layer (2-5 micrometers) is formed on a glass substrate. A transcription mold is removed after pushing a transcription mold (the pitch of 5-50 micrometers, a depth of 0.1-3 micrometers of a crevice, internal angle-of-inclination-18-18 degree) against

an unhardened photosensitive resin layer (30 - 50 kg/cm² x 30 seconds - 10 minutes). It irradiates with ultraviolet rays from the rear-face side of a glass substrate (more than 50 mJ/cm²), and a photosensitive resin layer is stiffened. It heats using heating apparatus (more than about [240 °C x 1 minute), and a photosensitive resin layer is calcinated. Finally,

aluminum is formed on the surface of a photosensitive resin layer, and a reflector is completed. There are the following problems in this manufacturing method.

[0016] The photosensitive resin layer of the thin film which removed the solvent from the applied photopolymer liquid and was formed has not hardened, and the resin layer with an uncured state has insufficient film properties (hardness, intensity, etc.), and by minute mold aggressiveness of the transcription mold of shape. Destruction of a thin film, form collapse, exfoliation, etc. take place, and concave-shaped size enlargement is difficult. When carrying out die pressing and removing a next transcription mold from an unhardened photosensitive resin layer, die releasing of a photosensitive resin layer is bad, and destruction of the same resin layer, form collapse, exfoliation, etc. take place. Since a hardened type photorealist system photopolymer generally has the large rate of cure shrinkage, the accurate size enlargement as a design is difficult. A heat-resistant system photopolymer (for example, inide system photorealist) also has the problem of generating a by-product (for example, water) in heat cure reaction time.

[0017] In [for example] the patent documents 8 in the field of a diffraction grating. (A) Polymethacrylate urethane denaturation polyester. (meta-) acrylate (700 or more molecular weights); -- 25 to 45 % of the weight (B) polyfunctional (meta-) acrylate (700 or more molecular weights); -- 31 - 50 % of the weight (C) monofunctional acrylate: -- the resin layer of the photocuring type resin composition which consists of 5 - a 44-% of the weight (D)

photopolymerization initiator being formed on a base, and, The diffraction grating in which the resin layer has repetition shape is proposed. An antireflection layer or a reflecting layer is formed in the surface. The resin layer which has repetition shape is fabricated by the casting method using molds, such as glass, metal, and a plastic, and it characterizes by the endurance of the obtained diffraction grating being excellent. There are the following problems in this manufacturing method.

[0018] Since both an ingredient (A) and an ingredient (B) are polyfunctional (meta) acrylate, their contraction at the time of photo-curing is large, and it is dramatically difficult to consider it as the minute shape as a design by cast molding. A molecular weight is large, durability test of an example is [only carrying out at 70 °C low temperature, and], and its heat resistance in an elevated temperature is poor as it is supposed that 700-5,000 (an example 860-3,000) are preferred as for the number average molecular weight of an ingredient (A).

[0019] [Patent documents 1] JP,6-16721,A[Patent documents 2] JP,6-263831,A[Patent documents 3]

JP,7-128503,A [Patent documents 4] JP,6-208008,A [Patent documents 5] JP,6-67004,A [Patent documents 6] JP,5-196808,A [Patent documents 7] JP,1-42649,A [Patent documents 8] JP,6-265710,A [0020]

[Problem(s) to be Solved by the Invention] The above-mentioned conventional known art can be classified as follows as a method of manufacturing the detailed size enlargement molded product which used the hardening resin constituent.

** Light or a manufacturing method made to heat-harden after pouring a hardening resin constituent into a die.

** Light or a manufacturing method which heat-hardens after pressing [or], dropping or applying a hardening resin constituent to a substrate, and pressing a size enlargement type.

** A manufacturing method which removes an uncured part after dropping or applying a hardening resin constituent to a substrate and carrying out photo-curing selectively through a photo mask.

[0021] In the above-mentioned manufacturing method of ** - **, since the rate of cure shrinkage is large, in the corner of design shape, a tip part, a part basillars ossis occipitals, etc., there is a common problem that it is dramatically difficult to carry out size enlargement of the precise shape as a design, and is easy to generate exfoliation with a substrate at the time of hardening, and distortion occurs in a hardened material. It is also difficult to obtain the molded product which has sufficient intensity and heat resistance.

[0022] At cast molding in the method of the above-mentioned **, since removal of the mixed air bubbles is almost impossible, the air bubbles which remained lead to the defect of a molded product, and serve as an important quality defect with the molded product of an optical application especially. In the method of the above-mentioned **, after applying a hardening resin constituent to a substrate, the solvent to contain in the resin (constituent) layer which is not hardened [which removed by evaporation etc. and was formed]. A metallic mold etc. are pressed, when transferring and carrying out size enlargement of the shape, the film properties (hardness, intensity, adhesion, etc.) of a resin (constituent) layer are insufficient, and serious problems, such as membranous destruction, shape collapse, and exfoliation, occur. The form collapse after pressing and carrying out size enlargement of the metallic mold etc. in an unhardened resin (constituent) layer is dramatically large, and since the die releasing becomes it is remarkable and poor especially in a detailed and precise mold, precise size enlargement is impossible.

[0023] This invention is made for the purpose of solving the problem of the above-mentioned conventional technology. Namely, the contraction at the time of hardening, the formation of incomplete full hard, cellular remains, and the film destruction at the time of size enlargement, Minute shape aims at providing the hardening resin constituent which can be manufactured simple for the detailed size enlargement molded product which has sufficient intensity by which

size enlargement was carried out good, and heat resistance, without generating problems, such as film peeling, shape collapse, and distortion.

[0024] Again this invention The contraction at the time of hardening, the formation of incomplete full hard, cellular remains, and the film destruction at the time of size enlargement, it aims at providing the detailed size enlargement molded product without problems, such as film peeling, shape collapse, and distortion, in which minute shape has sufficient intensity by which size enlargement was carried out good, and heat resistance, its manufacturing method, and the precision mechanical equipment with which this molded product was used.

[0025]

[Means for Solving the Problem] This inventions are a compound which has (A) allycyle fellows hydrocarbon skeleton and a radical polymerization nature group at least, and a hardening resin constituent consisting of a (B) polymerization initiator.

[0026] This invention is the precision mechanical equipment with which a detailed size enlargement molded product and this molded product, wherein it is obtained from the above-

mentioned hardening resin constituent, it uses a force piston for the hardened material surface again and size enlargement of the minute shape is carried out were used.

[0027] This invention is a manufacturing method of a detailed size enlargement molded product carrying out size enlargement of the minute shape to the hardened material surface, after making incomplete ** harden the above-mentioned hardening resin constituent thoroughly on a substrate further. In this invention, after making incomplete ** harden a hardening resin

constituent thoroughly in this way, since size enlargement is carried out, cure shrinkage does not affect size enlargement shape, but can carry out size enlargement of the minute shape as a design simple. Since size enlargement is carried out to a hardened film-like hardened material at the time of size enlargement of minute shape, serious problems, such as film destruction, film peeling, shape collapse, and distortion, are not generated at all, either. That is, all technical problems that a Prior art in a manufacturing method of a detailed size

enlargement molded product using a hardening resin constituent holds can be solved by this invention.

[0028] The artifice of this invention was able to find out that an above-mentioned method was applicable only to a hardening resin constituent which uses specific hardening resin as an ingredient, and were able to reach this invention.

[0029]

[Embodiment of the Invention] Fundamentally, the hardening resin constituent of this invention uses as an essential ingredient the compound (it is written as an ingredient (A) among this specification), which has (A) allycyle fellows hydrocarbon skeleton and a radical polymerization nature group, and the (B) polymerization initiator (it is written as an ingredient (B) among this specification). In this invention, as occasion demands, the compound (it is hereafter written as

an ingredient (A'), which has a radical polymerization nature group is used together with an ingredient (A) without having an alicycle (A') follows hydrocarbon skeleton.

[0030] The compound which is an ingredient (A) of "ingredient (A)" this invention has an alicycle follows hydrocarbon skeleton and a radical polymerization nature group. An alicycle follows hydrocarbon skeleton is a cyclic hydrocarbon skeleton which does not show aromatic property, there are 1 cyclic and a polycyclic type of 2 or more cyclic one, and a terpene skeleton and a steroid skeleton are also contained in a broad sense. The alicycle follows hydrocarbon skeleton may have a duplex or an unsaturated bond like a triple bond as hydrocarbon combination (carbon-carbon bonding which forms a ring), and may have a substituent like an alkyl group. An endocyclic carbon number (it is written as C_g) For example, C₆ expresses that the carbon number of a ring is 6. The following is also the same notation. It carries out, C₅ - C₁₂ are known, but chemically, C₅ - C₈ are stable and its alicycle follows hydrocarbon skeleton of C₅ - C₆ is especially preferred. When it illustrates with cyclic saturated hydrocarbon, specifically Cyclopentane, cyclohexane, A methylcyclohexane, ethylcyclohexane, 1 and 3, 5-dimethylcyclohexane, Bicyclo [1 cyclic alicycle follows hydrocarbon skeletons, such as dicyclohexyl, dicyclohexyl methane, 2,2-dicyclohexyl propane, tricyclohexyl methane

cycloheptane, and cyclooctane, [2, 1, 1]Bicyclo [hexane, [4, 1, 0]Bicyclo [heptane, [2, 2, 1] Bicyclo [heptane (norbornane), [3, 2, 1]Bicyclo [octane, [4, 2, 0]Bicyclo [octane, [4, 3, 0] Bicyclo [nonane, [4, 4, 0]Bicyclo [Decan (decahydronaphthalene), [4, 2, 2]2 cyclic alicycle follows hydrocarbon skeletons, such as Decan, tricyclo [5, 2, 1, 0, 2, 6] Decan, tricyclo [3, 3, 1, 1, 3, 7] Decan (adamantane), methyladamantane, tricyclo [6, 2, 1, 0, 2, 7] 3 cyclic alicycle follows hydrocarbon skeletons, such as an undecane, tetracyclo [6, 2, 1, 1, 3, 6, 0, 2, 7] There are 4 cyclic alicycle follows hydrocarbon skeletons, such as a dodecane.

[0031] In the above-mentioned alicycle follows hydrocarbon skeleton, if it chooses from the formativeness of minute shape, the thing of 2 or more cyclic ones which has bulky molecular structure is preferred, and the thing of 3 or more cyclic one is more preferred. The compound which has a 1 cyclic alicycle follows hydrocarbon skeleton is effectively used as reactive diluent of the compound which has a polycyclic type alicycle follows hydrocarbon skeleton of 2 or more cyclic one.

[0032] The radical polymerization nature group which the compound which is an ingredient (A) of this invention has is a basis which contains the unsaturated bond which can carry out a radical polymerization with either an optical exposure or heating under existence of a photopolymerization initiator or a thermal polymerization initiator. Specifically as such a radical polymerization nature group (meta), they are an acrylyl group (meta), an acrylamide (meta) group, and a vinyl group (an allyl group and a meta-allyl group are included.). The following is also the same. An ethynyl group, an isopropenyl group, a vinyl ether group, a vinyl thioether group, a

vinyl ketone group, a vinyl ester group, a vinylamino group, etc. are mentioned. the notation of this detailed in the letter one, an acrylyl group (meta-), an acrylamide (meta-) group, etc. includes and means "an acrylyl group and a methacryloyl group", and "an acrylamide group and a methacrylamide group", respectively.

[0033] As for the compound of an ingredient (A), it is preferred to have a radical polymerization nature group in [two or more] a molecule, and two or more radical polymerization nature groups are chosen from the group of the above-mentioned radical polymerization nature group. The film property or heat resistance to which size enlargement of the radical polymerization nature group is carried out in use of only one compound will not necessarily become sufficient. Even if they differ, respectively, and two or more radical polymerization groups which it has in the same molecule are the same, they are not cared about. The compound which has one radical polymerization nature group can be effectively used as reactive diluent.

[0034] From a viewpoint of hardenability (polymerization nature) or the physical properties of a hardened material, two or more desirable radical polymerization nature groups, (Meta) it is chosen from the group which consists of an acrylyl group, an acrylamide (meta) group, a vinyl group, a vinyl ether group, and a vinyl ester group, and is chosen from the group which consists of an acrylyl group (meta), an acrylamide (meta) group, and a vinyl group more preferably.

[0035] In the compound which is an ingredient (A) of this invention, the allycyclic follows hydrocarbon skeleton and the radical polymerization nature group may be connected directly, and, or -O-, -CH₂O-, -(CH₂)²O-, -O(CH₂)²O-, -O(CH₂)³O-, -OCH₂CH(CH₃)O-, and, it may be indirectly connected by connecting groups, such as O(CH₂)⁴O-, -OCH₂CH(OH)CH₂O-, -CH₂-, -(CH₂)²-, and -(CH₂)³-. If the number of carbon atoms of a connecting group becomes seven or more, since a problem will appear in detailed formativeness or heat resistance, it is not desirable.

[0036] Even if small among the compounds which have the above-mentioned allycyclic follows hydrocarbon skeleton and a radical polymerization nature group as an ingredient (A) of this invention Preferred allycyclic [2 or more] The polycyclic type allycyclic follows hydrocarbon skeleton of 3 or more cyclic one, it is preferred to use the compound which has the two or more above-mentioned radical polymerization nature groups" (it is hereafter written as a compound (a1)). At this time, "The compound which has a 1 cyclic allycyclic follows hydrocarbon skeleton and one or more radical polymerization nature groups." (it is hereafter written as a compound (a2).) - when using it effectively as reactive diluent, the compounding ratios of a compound (a1) and a compound (a2) are 100:0-60:40 (weight section), and are 100:0-70:30 (weight section) preferably.

[0037] In this invention, "The compound which has an allylic hydrocarbon skeleton of a polycyclic type, and one radical polymerization nature group," (it is hereafter written as a compound (a3)) -- when using it effectively as reactive diluent, the compounding ratios of a compound (a1) and a compound (a3) are 100:0-60:40 (weight section), and are 100:0-65:35 (weight section) preferably.

[0038] The compound which does not have an allylic hydrocarbon skeleton and has a radical polymerization nature group in "ingredient (A)" this invention as described above when the adjustment and improvement in the viscosity control of the hardening resin constituent of this invention or the physical properties of a hardened material are required (an ingredient (A)) may be used together. Compounds, such as an aliphatic series system which has the above-mentioned radical polymerization nature group as a compound of such an ingredient (A), for example, an aromatic system, and a heterocyclic system, are mentioned, also in an ingredient (A), use of the compound which has two or more bases chosen from the group which consists of an acrylyl group, an acrylamide (meta-) group, and a vinyl group as (meta-) a radical polymerization nature group is preferred.

[0039] (Meta) As an example of an aliphatic series system compound of having two or more acrylyl groups, Ethylene-glycol-di(metha)acrylate, 1, and 2- and 1, 3-propyleneglycol di(metha)acrylate, 1, 4-butanediol di(metha)acrylate, neopentyl glycol di(metha)acrylate, GURISERINJ (meta) acrylate, trimethylethane tri(metha)acrylate, TORIMECH roll pro panty (meta) acrylate, penta ERIS RITORULTORI (meta) acrylate, Pentaerythritol tetra (meta) acrylate, ditrimethylol propane tetra (meta) acrylate, The Tori (meta) acrylic acid adducts of dipentaerythritol hexa (meta) acrylate, trimethylolpropane triglycidyl ether, The Tori (meta) acrylic acid adducts of glycerol triglycidyl ether, the tetra (meta) acrylic acid adducts of pentaerythritol tetraglycidyl ether, the tetra (meta) acrylic acid adducts of ditrimethylol propane tetraglycidyl ether, The hexa (meta) acrylic acid adducts of dipentaerythritol hexa glycidyl ether, etc. are mentioned.

[0040] (Meta) As an example of an aromatic system compound of having two or more acrylyl groups, Ethyleneoxide and propylene oxide addition di(metha)acrylate of bisphenol A and F, The biphenyl 4, 4' - di(metha)acrylate and diphenyl ether 4 and 4'-di(metha)acrylate, A 9,9-bis[4-(metha)acryloyloxy phenyl]fluorene, A 9,9-bis[4-(meta) acryloyl ethoxyphenyl] fluorene, Bisphenol A and the JI (meta) acrylic acid adducts of F diglycidyl ether, The JI (meta) acrylic acid adducts of bisphenol A, F screw (glycidyl)oxy ethyl ether, and a screw (glycidyl) propyl ether, Biphenyl and the 3,5,3',5'-tetramethyl biphenyl 4, the JI (meta) acrylic acid adducts of 4'-diglycidyl ether, The naphthalene-1, the JI (meta) acrylic acid adducts of 6-diglycidyl ether, The Tori (meta) acrylic acid adducts of triphenylmethane 4,4',4"-triglycidyl ether, the tetra (meta) acrylic acid adducts of 1,2-tetrakis (p-glycidyl phenyl ether) ethane, The JI (meta) acrylic acid adducts of a 9,9-bis(p-glycidyl phenyl ether)fluorene, etc. are mentioned.

[0041] (Meta) As an example of a heterocyclic system compound of having two or more acrylyl groups, A 1,4-*l*-l (meta) acryloyl piperazine, 2,4-*l*-l (meta) acryloyl 5,5-dimethylhydantoin, 1,3,5-Tor (meta) acryloyl hexahydrotriazine, screw [2-(meta) acryloyloxyethyl]-[2-hydroxyethyl] isocyanurate, Tris [2-(meta) acryloyloxyethyl] isocyanurate, 2, the *l*-l (meta) acrylic acid adducts of 4-diglycidyl 5,5-dimethylhydantoin, The Tor (meta) acrylic acid adducts of triglycidyl isocyanurate, 2,4,6-tris (dihydroxy methylamino)-1,3,5-triazine hexa (meta) acrylate, etc. are mentioned.

[0042] (Meta) As an example of a compound of having two or more acrylamide groups, N,N-methylethenebis (meta) (acrylamide), 1,4-(meta) (acrylamide methyl) phenylene, etc. are mentioned.

[0043] As an example of a compound of having two or more vinyl groups, *m*- and *p*-divinylbenzene, bis(4-allyloxy phenyl)propane, 1,5-diallyl-3-propyl isocyanurate, 2,4,6-tris (vinylmethoxy)-1,3,5-triazine, 1,3,5-Tor (meta) allyl isocyanurate, etc. are mentioned.

[0044] The oligomer system compound which is low molecular weight polymer which has two or more bases chosen from the group which consists of an acrylyl group (meta-), an acrylamide (meta-) group, and a vinyl group as a compound of an ingredient (A') can also be used. As oligomer, polyphenol condensates, such as a novolac type, a polyester oligomer, polyether oligomer, polyurethane oligomer, etc. are mentioned.

[0045] As a radical polymerization nature group, as an oligomer system compound which has two or more acrylyl groups (meta), Phenol, cresol, bisphenol A, and the poly (meta) acrylic acid adducts of the novolac type polyphenol condensate of diphenol, The poly (meta) acrylic acid adducts of a tris(hydroxyphenyl) methane condensate, Bisphenol A and the *l*-l (meta) acrylic acid adducts of the condensate of F and epichlorohydrin, the poly (meta) acrylate of an aromatic system polyester oligomer, the poly (meta) acrylate of aromatic system polyurethane oligomer, etc. are mentioned.

[0046] As an ingredient (A'), the compound which has compatibility to an ingredient (A) is independently used for two or more kinds also in the above-mentioned compound, combining. When using it combining two or more kinds of compounds, it is preferred to choose the compound of each other with good compatibility. This invention -- setting -- an ingredient (A') -- loadings -- an ingredient -- (A --) -- an ingredient (A') -- a total amount -- 30 -- % of the weight -- less than -- desirable -- 20 -- % of the weight -- less than -- it is.

[0047] The polymerization initiator which is an ingredient (B) or "ingredient (B)" this invention is an essential ingredient for stiffening the hardening resin constituent of this invention. As an ingredient (B) of this invention, a photopolymerization initiator (it is hereafter written as an ingredient (B1)) or/and a thermal polymerization initiator (it is hereafter written as an ingredient (B2)) are used. It depends for selection of a polymerization initiator on a curing method. When making it face to harden the hardening resin constituent of this invention in detail and

performing photo-curing independently, a photopolymerization initiator (ingredient (B1)) is blended independently, When performing heat curing independently, a thermal polymerization initiator (ingredient (B-2)) is blended independently, and when carrying out combining photocuring and heat curing, a photopolymerization initiator (ingredient (B1)) and a thermal polymerization initiator (ingredient (B-2)) combine, and are blended.

[0048]ingredient (B1)

The photopolymerization initiator which is an ingredient (B1) of this invention is an essential ingredient for stiffening the hardening resin constituent of this invention by optical exposure. Of course, when making it harder by electron beam irradiation, it is unnecessary, but as a curing method, it is dramatically expensive, and, generally hard to adopt.

[0049]As a photopolymerization initiator (ingredient (B1)), there is no compound which is limited to this invention. The photopolymerization initiator currently generally used, i.e.,

acetophenones, and benzophenones. Diacetyl, benzyl, benzoin, benzoin ether, Benzyl dimethyl ketal, benzoyl benzoate, and hydroxyphenyl ketone. All of organophosphorus compound system photopolymerization initiators, such as organosulfur compound system photopolymerization initiators, such as carbonyl compound system photopolymerization initiators, such as aminophenyl ketone, CHIRALUM sulfide, and thioxan ions, acyl phosphine oxide, and acyl phosphinate, etc. can use it. In this invention, the photopolymerization initiator of such various sorts is independently used combining two or more kinds.

[0050]The loadings of a photopolymerization initiator (ingredient (B1)) are 1 - 8 weight section preferably 0.5 to 10 weight section to total amount 100 weight section of an ingredient (A) and an ingredient (A). Since loadings become poor [a photoresist] in less than 0.5 weight section and become insufficient [the film strength of a hardened material], size enlargement of the detailed shape cannot be carried out precisely, but poor size enlargement, such as film destruction, film peeling, and shape collapse, happens. If a compounding ratio exceeds ten weight sections, since it will have influence bad to the film property of a hardened material in which a hardening reaction becomes rapid too much, it is not desirable.

[0051]ingredient (B-2)

The thermal polymerization initiator which is an ingredient (B-2) of this invention is an essential ingredient for stiffening the hardening resin constituent of this invention with heat. Not less than about 30 ° or not less than about 60 ° thermal polymerization initiators are preferably used for pyrolysis temperature among the thermal polymerization initiators which decompose with heat and generate a radical as a thermal polymerization initiator (ingredient (B-2)). Especially use of the organic peroxide which does not generate a by-product like [among the compounds generally used as a thermal polymerization initiator of a radical polymerization reaction from the former] a gas or water as such a thermal polymerization initiator is preferred. If pyrolysis temperature uses the thermal polymerization initiator below about 30 °, since the resin

peroxide can be used in this invention.

[0053] The loadings of a thermal polymerization initiator (B-2) are 1 - 4 weight section preferably 0.5 to 5 weight section to total amount 100 weight section of an ingredient (A) and an ingredient (A'). Since loadings become poor [thermosetting] in less than 0.5 weight sections and become insufficient [the film strength of a hardened material], size enlargement of the detailed shape cannot be carried out precisely. If a compounding ratio exceeds five weight sections, since a hardening reaction will become rapid too much and destruction and exfoliation of a hardened material will occur, it is not desirable. In this invention, it may be used combining two or more kinds of organic-acid-peroxide-izing.

[0053] The compound which has one radical polymerization nature group in intramolecular may be further blended with the hardening resin constituent of reactive diluent this invention as reactive diluent without having an allylic fellow hydrocarbon skeleton. Reactive diluent is blended when the viscosity of a resin composition, hardenability and formativeness, the physical properties of a size enlargement molded product, etc. need to be adjusted. As such a compound, as for the radical polymerization nature group which it has one piece in intramolecular, in order to make a photoreist and thermosetting equivalent to an ingredient (A) as much as possible, it is preferred that they are especially an acrylyl group (meta), an

[0056](Meta) As a compound which has one acrylyl group, For example, n-, i- and t-butyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, Methoxy ethylene glycol (meta) acrylate, phenyl (meta) acrylate, Phenoxyethyl (meta) acrylate, benzyl (meta) acrylate, Biphenyl (meta) acrylate, o-, m-, and p-phenyl (meta) acrylate, o-, m- and p-phenylbenzyl (meta) acrylate, 1-naphthyl (meta) acrylate, Tetrahydrofurfuryl (meta) acrylate, furfuryl (meta) acrylate, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, dimethyl and diethylaminoethyl (meta) acrylate, N-(meta) acryloyl morpholine, etc. are mentioned.

http://www4.ipdl.inpiti.go.jp/cgi-bin/tran_web/cgi_ejje?atw_u=http%3A%2F%2Fwww4.ipd... 5/6/2009

[0059]Also in such reactive diluent, especially the thing for which the boiling point uses not less than 150 °C especially not less than 200 °C reactive diluent from the viscosity and stability of the hardening resin constituent of this invention, the formativeness of a hardened material, etc. is preferred.

[0060]As for the loadings of reactive diluent, 10 or less % of the weight is usually preferred to the total amount of an ingredient (A) and an ingredient (A'). It may be used combining two or more kinds of reactive diluent.

[0061]A solvent may be blended with the hardening resin constituent of solvent this invention in order to reduce the viscosity of a resin composition. However, the solvent needs to carry out evaporation removal, photo-curing or before heat-hardening. As a solvent, there are aliphatic series, allylic series, aromatic system hydrocarbon, alcohol, ester species, ether, ester

[0062]As an example of hydrocarbon, for example N-octane, n-nonane, n-Decane, 2,2,5-trimethyl hexane, cyclohexane, ethylcyclohexane, Decalin, toluene, o-, m- and p-xylene, ethylbenzene, cumene, mesitylene, n-, sec- and t-butylbenzene, p-cymene, o-, m-, and p-diethylbenzene etc. are mentioned.

[0063]As an example of alcohols, for example n- and i-butanol, 1-, 2- and 3-pentanol, 2-methyl-1-butanol, i-pentyl alcohol, 3-methyl-2-butanol, neopentyl alcohol, 1-hexanol, 1-, 2- and 3-heptanol, 1- and 2-octanol, a 2-ethyl-1-hexanol, cyclohexanol, 2-, 3- and 4-methyl

cyclohexanol, 1,2-ethanediol, a 1,2-propanediol, etc. are mentioned.

[0064]As an example of ester species, for example Acetic acid-n-, i-, and -sec-butyl, Acetic acid-n- and -i-pentyl and acetic acid-n- and -sec-hexyl, acetic acid-2-ethylhexyl, cyclohexyl acetate, cyclohexyl acetate, propionic acid-n-butyl, ethyl butyrate and -n-butyl, ethylene glycol diacetate, etc. are mentioned.

[0065]As an example of ether, for example Di-n-butyl ether, an anisole, Phenetyl, methoxy-o-, -m-, and -p-toluene, benzyl ethyl ether, ethylene glycol diethylether, diethylene glycol dimethyl ether, diethylene-glycol diethylether, etc. are mentioned.

[0066]As an example of ether alcohol, for example Ethylene glycol monomethyl ether, Ethylene glycol monoethyl ether and ethylene glycol mono-n- and -i-propyl ether, Ethylene glycol mono-n-butyl ether, diethylene glycol monomethyl ether, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, etc. are mentioned.

[0067]As an example of ester alcohols, ethylene glycol mono- acetate, ethylene glycol mono-n-propionate, glycerol monoacetate, etc. are mentioned, for example.

[0068]As an example of ester ether, ethylene glycol methyl ether acetate, ethylene glycol ethyl ether acetate, ethylene glycol n-butyl ether acetate, etc. are mentioned, for example.

[0069]As an example of ketone, 2- and 3-hexanone, methyl-t-butyl ketone, 2-, 3- and 4-

[0071] As the boiling point of a solvent, the range of 100-200 °C is preferred. Since it is easy to evaporate the boiling point in less than 100 °C, it is difficult to maintain the solvent amount in the hardening resin constituent of this invention, and it cannot keep viscosity of a resin composition resistant easily. If the boiling point exceeds 200 °C, evaporation removal is conversely difficult, and since it becomes easy to remain in a resin composition and a hardened material, it is not desirable.

[0074] Since size enlargement is carried out after facing manufacturing a detailed size enlargement molded product from the hardening resin constituent of above-mentioned this invention and hardening to incomplete ** thoroughly, Minute shape can provide the detailed size enlargement molded product which has sufficient intensity by which size enlargement was carried out good, and heat resistance, without generating problems, such as the contraction at the time of hardening, cellular remains and film destruction at the time of size enlargement, film peeling, shape collapse, and distortion. Methods of manufacturing a detailed size enlargement molded product from the hardening resin constituent of this invention include the following two-

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[0076] Although the spreading board in particular is not restricted, the glass substrate which is excellent in heat resistance or surface smoothness is preferred. The surface treatment of the surface of a glass substrate may be carried out using a coupling agent or a primer.

[0077] What kind of method may be adopted as evaporation removal of a solvent -- for example, after spreading, a room temperature, or warming -- the method of neglecting it under ordinary pressure or decomposition in the bottom, etc. are mentioned. the case where the thermal polymerization initiator (ingredient (B-2)) is blended -- warming -- it is necessary to make temperature into less than the decomposition temperature of a thermal polymerization initiator [0078] Although the coating film thickness before hardening changes also with uses of a molded product, generally it is the range of number -100micrometer. A glass substrate may be used only for one side, and may be used for rear surface both sides. In the case of both sides, a glass substrate is put on the coating film surface after solvent removal.

[0079] Next, photo-curing or heat curing is independently performed to the coating film on a substrate, or it carries out combining photo-curing and heat curing, and is made to harden thoroughly. If photo-curing or heat curing is performed independently and stiffened thoroughly, since it ends with one step of curing processes, it is advantageous as a result. Generally, since photo-curing is excellent in handling nature, a cure rate, etc. compared with heat curing, in this invention, photo-curing is performed independently, and the method of carrying out complete cure is advantageous.

[0080] In the case of the photo-curing which blended the photopolymerization initiator (ingredient (B1)), irradiating with ultraviolet rays is common. As a light source of ultraviolet rays, although there are an ultrahigh pressure mercury lamp, a high-pressure mercury-vapor lamp, a low pressure mercury lamp, metal halide light, a carbon arc lamp, xenon light, etc., use of a high-pressure mercury-vapor lamp or metal halide light is preferred. When performing photo-curing independently and carrying out complete cure, the amount of UV irradiation changes also with ingredient composition of a hardening resin constituent, but it is usually 2,500 - 5,000 mJ/cm².

[0081] In the case of heat curing which blended the organic peroxide (ingredient (B-2)) which is a thermal polymerization initiator, it heats more than the pyrolysis temperature of the above mentioned organic peroxide, and it is stiffened. Cooking time is usually for 10 to 60 minutes. [0082] In hardening which combined the photo-curing which blended both organic peroxide (ingredient (B-2)) with the photopolymerization initiator (ingredient (B1)), and heat curing, it is common to heat-harden with heating first, after carrying out photo-curing by UV irradiation. In this case, even if it does not carry out complete cure of the coating film by photo-curing, complete cure can be carried out according to continuing heat curing. The above-mentioned heating conditions may be sufficient as the heating.

[0083] Since the hardened state of the hardening layer after photo-curing or/and heat curing

can be measured using a Fourier-transform-infrared-spectroscopic-analysis device, a photochemical reaction calorimeter, etc., the curing conditions, as for, the hardening resin constituent of this invention carries out complete cure can be selected suitably.

[0084] Then, if size enlargement of the detailed shape is carried out to the hardening layer surface obtained by the above-mentioned curing method using a force piston, a detailed size enlargement molded product will be fabricated. It releases from mold, after pressing against a hardening layer the force piston which has detailed shape and making a hardening layer transfer the minute shape of a force piston, holding in detail the substrate with which the hardening layer was formed to a heated state. In this invention, the hardening layer can carry out size enlargement of the detailed shape good, without causing the exfoliation from a substrate, destruction or shape collapse of size enlargement, etc., since it has a good film property which size enlargement is easy to be carried out even if complete cure is carried out. The mold-release characteristic of the force piston after size enlargement is also good. Size enlargement is carried out under a heated state in order to soften a little hardening layer and to make size enlargement easier.

[0085] Although the detailed size enlargement conditions by a force piston change also with component composition of the resinsous principle (an ingredient (A) or an ingredient (A), and an ingredient (A')) of the hardening resin constituent of this invention. Usually, a pressure is 200 - 300MPa preferably 100 to 400 MPa under the cooking temperature at 200-300 **, and 150-300 ** of time is 20 to 50 seconds preferably for 5 to 60 seconds.

[0086] (Method 11) After carrying out photo-curing (formation of incomplete full hard) of the coating film moderately and carrying out size enlargement to an incomplete full hard-sized membrane surface as a manufacturing method of another detailed size enlargement molded product of this invention, it is the method of carrying out complete cure according to heat curing. This method has the feature in size enlargement conditions [****] being employable rather than the case of a complete cure film.

[0087] The coating film first formed on the substrate is made to form into incomplete full hard by ultraviolet rays like the method 1 in detail. The adhesiveness of the surface of a hardening layer is lost, and if it becomes film destruction, film peeling, and a film property that shape collapse does not generate at the time of size enlargement, photo-curing will be stopped by this photocuring. Since the incomplete full hard-sized film has a good film property which size enlargement is easy to be carried out, it can carry out size enlargement of the detailed shape precisely. The amount of UV irradiation is the range of 500 - 2000 mJ/cm², and should just usually choose an optimal condition.

[0088] Subsequently, size enlargement of the detailed shape is carried out to an incomplete full hard-sized film using a force piston. That is, it releases from mold, after pressing against an incomplete full hard-sized film the force piston which has detailed shape and making the minute

shape of a force piston transfer, holding the substrate with which the incomplete full hard-sized film was formed to a heated state. Without causing the exfoliation from a substrate, destruction or shape collapse, etc., since it has a good film property which size enlargement is easy to be carried out, the incomplete full hard-sized film can carry out size enlargement of the detailed shape good, and its mold-release characteristics of the force piston after size enlargement is also good.

[0089] Also in this method, size enlargement processing is carried out under a heated state in order to soften a little incomplete full hard-sized film and to make size enlargement easier. In this method, the thermal polymerization initiator is blended with the photopolymerization initiator into the hardening resin constituent. Since size enlargement is carried out holding to a heated state, as a thermal polymerization initiator, combination of pyrolysis type organic peroxide is preferred.

[0090] The application-of-pressure time of the detailed size enlargement conditions by a force piston is enough in several seconds - 20 seconds under the cooking temperature at 100-150 **, low pressure may be comparatively sufficient as a pressure, and it is usually the range of 50 - 200MPa.

[0091] Complete cure of the incomplete full hard-sized film by which size enlargement was carried out to the last is carried out with heat. That is, the radical polymerization nature group which remains in the incomplete full hard-sized film by which size enlargement was carried out is thoroughly stiffened by heating. For this reason, there is almost no cure shrinkage of the complete cure film by heat cure by which size enlargement was carried out, size enlargement shape is held as it is, and it can be considered as the size enlargement molded product which was moreover excellent in heat resistance. Neither shape collapse of a size enlargement molded product, nor exfoliation, destruction, etc. are generated. Although heating conditions change with kinds, loadings, etc. of organic peroxide, cooking temperature is 150-250 **, and cooking time is usually for a number - 60 minutes.

[0092] The detailed size enlargement molded product of this invention manufactured in accordance with the above methods 1 and the method 11 does not have problems, such as the contraction at the time of hardening, cellular remains and film destruction at the time of size enlargement, film peeling, shape collapse, and distortion, and shape with a detailed force piston is transferred with sufficient accuracy. Although there is no restriction in particular, even if the depth (height) and width (pitch) are the detailed shape of several micrometers, size enlargement of the minute shape of a force piston is carried out by the extremely outstanding transfer rate of not less than 95%. Softening temperature is not less than 250 **, and the detailed size enlargement molded product of this invention has the outstanding heat resistance. For example, even if it heats a detailed size enlargement molded product at 250 **

for 1 hour, modification, shape collapse, destruction, exfoliation, etc. do not take place, but are excellent also in the shape reactivity in an elevated temperature. Therefore, under high temperature service, with conventional methods, such as vacuum deposition, sputtering process, and the ion plating method, even if it vapor-deposits a metal thin film to a size enlargement molded product, detailed shape does not change into it. The detailed size enlargement molded product of this invention is excellent also in adhesion with intensity or a substrate.

[0093] The detailed size enlargement molded product manufactured using the hardening resin constituent of this invention, Taking advantage of the feature which was described above, as parts and members, such as a Fresnel lens, a lenticular lens, a micro lens, a prism sheet, a light reflection plate, an optical diffusion board, and a diffraction grating, it can be used for a variety of precision mechanical equipments, such as an optical instrument, liquid crystal display device, projection apparatus, and optical communication equipment. Although the following examples explain this invention more concretely, this invention is not limited to an example.

[0094]

[Example] An examination and measurement followed the method of carrying out the account of following.

< size enlargement examination: the section with a distance between tips of 2 micrometers did the size enlargement processing examination by aggressiveness pressing down on the surface (Examples 1-4 and the comparative example 1 - 3.0 mm by [7<] 3.0 mm x 1.0 mm in thickness) using the size enlargement public-funds type which arranged triangular convex form shape in a depth of 1 micrometer. On the smooth glass substrate, the surface with a 50 mm by 50 mm x thickness of 0.7 mm applied the hardening resin constituent of the specified quantity, in the case of the resin composition containing a solvent, evaporation removal of the solvent was carried out, and it formed the coating film of the resin composition. Next, it irradiated with the ultraviolet rays which use metal halide light (Co., Ltd. excels and it does not come out form UVC-301W) as a light source until it became a predetermined dose from the surface side of a resin composition coating film, and photo-curing of the coating film was carried out. It was made to heat-harden on condition of further predetermined as occasion demands.

independent, after applying a hardening resin constituent on a glass substrate according to the same procedure and conditions as the above, it was made to heat-harden by photo-curing the hardening layer was obtained. This piece of a hardening layer blank test was cut off, and it measured using the Fourier-transform-infrared-spectroscopic-analysis device (the product made by Perkin-Elmer: System2000), and the photochemical reaction calorimeter (Seiko Instruments make: form PDC121), and checked that a hardening layer was in a complete cure state. After having attached the glass substrate and size enlargement

public-funds type which were covered with this hardening resin film between hot platens, carrying out size enlargement processing in the center section of the hardening resin membrane surface in aggressiveness pressing down, and a predetermined, predetermined temperature and time and releasing a metallic mold from mold, it took out from between hot platens. The sensing pin type surface unevenness meter (the product made by KLA Tencor: form HRP-100) was used for the rectangular directions of the arrangement of 0.5 mm of center sections of the size enlargement portion of a hardening resin membrane surface of triangular shape, and the size enlargement state of triangular shape was measured. The transfer rate measured value of the depth direction of size enlargement.

[0095] < size enlargement examination; instead of performing example 5 > photo-curing, the size enlargement examination was done like the described method after example 6 > size enlargement except having performed check of hardening layer being in a complete cure state, and measurement of the transfer rate after heat curing.

[0097] < Example 1 > dimethylol tricyclo [5.2,1,0²,⁶] Decan dimethacrylate: 7.0 g, 1, 4-cyclohexane dimethanol dimethacrylate: 3.0g, and IRGACURE 907 (Tiba Specialty Chemicals products): 0.80 g was mixed, it dissolved, and hardening resin constituent (1) was prepared. This resin composition (1) was applied on the glass substrate using the spin coater. The thickness of the coating film of resin composition (1) was 4 micrometers. This coating film was irradiated with ultraviolet rays until it became 3,600 mJ/cm², and it was considered as the photo-curing resin layer. The photo-curing resin layer checked carrying out complete cure by the above-mentioned measurement. Next, using the size enlargement public-funds type, in 270 **, size enlargement was carried out to the surface of the photo-curing resin layer, and the metallic mold was released from mold under the application of pressure of 250MPa for 30 seconds. The mold-release characteristic of the metallic mold was good. The result of having measured the transfer rate of size enlargement is 95%, and obtained the very good value.

[0098] Dimethylol tricyclo in the < comparative example 1 > example 1 [5.2,1,0²,⁶] instead of Decan dimethacrylate, except using methacrylic acid 2 mol addition: 7.0g of bisphenol A diglycidyl ether, an equivalent amount of the same ingredients as Example 1 were blended, and the hardening resin constituent (1) was prepared. According to the same procedure and conditions as Example 1, the photo-curing resin layer by which size enlargement was carried out to glass substrate Kami was obtained using this resin composition (1). Complete cure of

the photo-curing resin layer before a size enlargement examination was carried out. The result of having measured the transfer rate of size enlargement was as low as 55%, and triangular shape had collapsed.

[0099]Dimethyloletricyclo in the <comparative example 2> example 1 [5.2, 1.0², 6] instead of Decan dimethacrylate, except using trimethylopropanetrimethacrylate: 7.0g, an equivalent amount of the same ingredients as Example 1 were blended, and the hardening resin constituent (2) was prepared. According to the same procedure and conditions as Example 1, the photo-curing resin layer by which size enlargement was carried out to glass substrate Kami was obtained using this resin composition (2). Complete cure of the photo-curing resin layer before a size enlargement examination was carried out. The result of having measured the transfer rate of size enlargement was as low as 20%, triangular shape has collapsed, and film destruction and film peeling were also seen.

[0100]Dimethyloletricyclo in the <comparative example 3> example 1 [5.2, 1.0², 6] instead of Decan dimethacrylate, except using tris(2-hydroxyethyl) isocyanurate: 7.0g, an equivalent amount of the same ingredients as Example 1 were blended, and the hardening resin constituent (3) was prepared. According to the same procedure and conditions as Example 1, the photo-curing resin layer by which size enlargement was carried out to glass substrate Kami was obtained using this resin composition (3). Complete cure of the photo-curing resin layer before a size enlargement examination was carried out. The result of having measured the transfer rate of size enlargement was as low as 35%, triangular shape has collapsed, and film destruction was also seen.

[0101]<Example 2> dimethyloletricyclo [5.2, 1.0², 6] Decan dimethacrylate: Bicyclo [6.0 g, / 4-methyl-7,7-dimethyl] [2.2, 1.0², 6] Heptanylmethacrylate (isobornyl methacrylate): 3.0 g, Trimethylopropanetrimethacrylate: 1.0 g, IRGACURE 907(above): 0.4g and 1173(Tiba Specialty Chemicals products): 0.3 g of DAROKYUA were mixed, it dissolved, and hardening resin constituent (ii) was prepared. This resin composition (ii) was applied on the glass substrate using the spin coater. The thickness of the coating film of resin composition (ii) was 5 micrometers. This coating film was irradiated with ultraviolet rays until it became 3,000 mJ/cm², and it was considered as the photo-curing resin layer. The photo-curing resin layer checked carrying out complete cure by the above mentioned measurement. Next, using the size enlargement public-funds type, in 250 **, size enlargement was carried out to the surface of the photo-curing resin layer, and the metallic mold was released from mold under the application of pressure of 200MPa for 30 seconds. The mold-release characteristic of the metallic mold was good. The result of having measured the transfer rate of size enlargement is 95%, and obtained the very good value.

[0102]Dimethyloletricyclo in the <comparative example 4> example 2 [5.2, 1.0², 6] instead of

Decan dimethacrylate, except using methacrylic acid 2 mol addition; 6.0g of bisphenol F diglycidyl ether, an equivalent amount of the same ingredients as Example 2 were blended, and the hardening resin constituent (4) was prepared. According to the same procedure and conditions as Example 2, the photo-curing resin layer by which size enlargement was carried out on the glass substrate was obtained using this resin composition (4). Complete cure of the photo-curing resin layer before a size enlargement examination was carried out. The result of having measured the transfer rate of size enlargement was as low as 45%, and triangular shape had collapsed.

[0103] Dimethylol tricyclo in the <comparative example 5> example 5 [5.2, 1.0², 6] instead of Decan dimethacrylate, except using dipentaerythritol hexamethacrylate; 6.0g, an equivalent amount of the same ingredients as Example 2 were blended, and the hardening resin constituent (5) was prepared. According to the same procedure and conditions as Example 2, the photo-curing resin layer by which size enlargement was carried out on the glass substrate was obtained using this resin composition (5). Complete cure of the photo-curing resin layer before a size enlargement examination was carried out. The result of having measured the transfer rate of size enlargement was dramatically as low as 35%, triangular shape collapsed, and film destruction was also seen.

[0104] The < example 3 > 1, 3-adamantanediol dimethacrylate (Kyoetsu Chemicals products) [5.2, 1.0², 6] - 2-deceny acrylate; 2.5 g, pentaerythritol trimethacrylate; 1.0g, and 1700 (Tribal Specialty Chemicals products); 0.7 g of IRGACURE were mixed, it dissolved, and the hardening resin constituent (iii) was prepared. This resin composition (iii) was applied on the glass substrate using the spin coater. The thickness of the coating film of resin composition (iii) was 7 micrometers. This coating film was irradiated with ultraviolet rays until it became 3,300 mJ/cm², and it was considered as the photo-curing resin layer. The photo-curing resin layer checked carrying out complete cure by the above mentioned measurement. Next, using the size enlargement public-fund type, in 230 **, size enlargement was carried out to the surface of the photo-curing resin layer under the application of pressure of 200MPa for 30 seconds, and the metallic mold was released from mold. The mold-release characteristic of the metallic mold was good. The result of having measured the transfer rate of size enlargement is 95%, and obtained the very good value.

[0105] Instead of [1 in the <comparative example 6> example 3, and 3-adamantanediol dimethacrylate] - 1, 3, and 5 - doria - except using KURIRORU hexahydro 1,3,5-triazine; 6.5g, an equivalent amount of the same ingredients as Example 3 were blended, and the hardening resin constituent (6) was prepared. According to the same procedure and conditions as Example 3, the photo-curing resin layer by which size enlargement was carried out on the glass substrate was obtained using this resin composition (6). Complete cure of the

photo-curing resin layer before a size enlargement examination was carried out. The result of having measured the transfer rate of size enlargement was dramatically as low as 40%, triangular shape collapsed, and film destruction and film peeling were seen.

[0106]<Example 4> dimethylol tricyclo [5.2.1.0^{2,6}] Decan dimethacrylate: -- 6.5 g and pentaeerythritol -- doria KURIRETO: -- 3.5 g, IRGACURE 907(above):0.3 g, cumene-

hydroperoxide:0.2g, and ethylene-glycol methyl-ether acetate: 10.0 g was mixed, it dissolved and the hardening resin constituent (IV) solution was prepared. This resin composition (IV)

solution was applied on the glass substrate using the spin coater. Then, it was neglected to room temperature, evaporation removal of the solvent heated and contained at 50 °C under

decompression for a while was carried out further, and the coating film of 3-micrometer-thick resin composition (IV) was obtained. This coating film was irradiated with ultraviolet rays until it became 2,500 mJ/cm², then it heated for 30 minutes at 120 °C, and was considered as light /

heat-curing resin layer. Light / heat-curing resin layer checked carrying out complete cure by the above mentioned measurement. Next, using the size enlargement public-funds type, in 250 °C, size enlargement was carried out to the surface of light / heat-curing resin layer under the

application of pressure of 250MPa for 30 seconds, and the metallic mold was released from mold. The mold-release characteristic of the metallic mold was good. The result of having

measured the transfer rate of size enlargement is 95%, and obtained the very good value. On the surface of the hardening resin film by which size enlargement was carried out, in

accordance with the conventional method, aluminum was vapor-deposited so that it might be set to about 0.1 micrometer in thickness, and on it, it was considered as the light reflection plate. When the shape of surface type of this light reflection plate was measured using the

sensing pin type surface unevenness meter, collapse of triangular shape was not seen at all. [0107]Dimethylol tricyclo in the <comparative example 7> example 4 [5.2.1.0^{2,6}] Instead of

Decan dimethacrylate, except using dimethacrylate:6.5g of 2 mol of bisphenol A ethyleneoxide addition, an equivalent amount of the same ingredients as Example 4 were

blended, and the hardening resin constituent (7) was prepared. According to the same procedure and conditions as Example 4, the light / heat-curing resin layer by which size

enlargement was carried out on the glass substrate were obtained using this resin composition (7). Complete cure of the light / the heat-curing resin layer before a size enlargement examination was carried out. The result of having measured the transfer rate of size

enlargement was dramatically as low as 50%, and triangular shape had collapsed.

[0108]<Example 5> dimethylol tricyclo [5.2.1.0^{2,6}] Decan dimethacrylate: -- 6.5 g and pentaeerythritol -- doria -- KURIRETO:3.5g, t-butyl hydroperoxide:0.2g, and ethylene glycol methyl ether acetate:10.0g were mixed, it dissolved, and the hardening resin constituent (V)

solution was prepared. This resin composition (V) solution was applied on the glass substrate

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using the spin coater. Then, it was neglected to the room temperature, evaporation removal of the solvent heated and contained at 50 °C under decompression for a while was carried out further, and the coating film of 3-micrometer-thick resin composition (V) was obtained. This coating film was heated for 20 minutes at 120 °C, and was used as the heat-curing resin layer. The heat-curing resin layer checked carrying out complete cure by the above mentioned measurement. Next, using the size enlargement public-funds type, in 250 MPa for 30 seconds, and the metallic mold was released from application of pressure of 250 MPa for 30 seconds, and the metallic mold was released from mold. The mold-release characteristic of the metallic mold was good. The result of having measured the transfer rate of size enlargement is 95%, and obtained the very good value. On the surface of the hardening resin film by which size enlargement was carried out, in accordance with the conventional method, aluminum was vapor-deposited so that it might be plate. When the shape of surface type of this light reflection plate was measured using the sensing pin type surface unevenness meter, collapse of triangular shape was not seen at all.

[Example 6] Dimethylol triethylol [5,2,1,0²,6] Decan dimethacrylate: -- 6.5 g and pentaerythritol -- doria KURIRETO: -- 3.5 g, IRGACURE 907 (above): 0.3 g, dicumylperoxide: 0.2 g, and ethylene-glycol methyl-ether acetate: 10.0 g was mixed, it dissolved and the hardening resin constituent (VI) solution was prepared. This resin composition (VI) solution was applied on the glass substrate using the spin coater. Then, it was neglected to the room temperature, evaporation removal of the solvent heated and contained at 50 °C under decompression for a while was carried out further, and the coating film of 3-micrometer-thick resin composition (VI) was obtained. This coating film was irradiated with ultraviolet rays until it became 1,200 mJ/cm², and it was considered as the photo-curing resin layer without adhesiveness. Next, using the size enlargement public-funds type, size enlargement was carried out to the surface of the photo-curing resin layer under the application of pressure of 180 MPa for 15 seconds at 140 °C, and the metallic mold was released from mold. The mold-release characteristic of the metallic mold was good. Then, it heated for 20 minutes at 200 °C, and was considered as the light / heat-curing resin layer by which size enlargement was carried out. The light / heat-curing resin layer by which size enlargement was carried out checked carrying out complete cure by the above mentioned measurement. The result of having measured the transfer rate of size enlargement is 95%, and obtained the very good value. On the surface of the hardening resin film by which size enlargement was carried out, in accordance with the conventional method, aluminum was vapor-deposited so that it might be plate. When the shape of surface type of this light reflection plate was measured using the sensing pin type surface unevenness meter, collapse of triangular shape was not seen at all.

and was considered as the light / heat-curing resin layer by which size enlargement was carried out. The light / heat-curing resin layer by which size enlargement was carried out checked carrying out complete cure by the above mentioned measurement. The result of having measured the transfer rate of size enlargement is 95%, and obtained the very good value. On the surface of the hardening resin film by which size enlargement was carried out, in accordance with the conventional method, aluminum was vapor-deposited so that it might be plate. When the shape of surface type of this light reflection plate was measured using the sensing pin type surface unevenness meter, collapse of triangular shape was not seen at all.

[0110]

[Effect of the invention] With the hardening resin constituent of this invention, the detailed size enlargement molded product in which size enlargement was improved minute shape by enlargement and which has sufficient intensity and heat resistance can be manufactured simple, without causing problems, such as the contraction at the time of hardening, the formation of incomplete full hard, cellular remains and film destruction at the time of size enlargement, film peeling, shape collapse, and distortion.

[Translation done.]